



Graphene nanoplatelets in titanium coatings deposited by cold spray: Mechanical properties

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ABSTRACT

Nano-platelets Graphene (GNPs) have emerged as a promising reinforcement for Ti coatings due to their exceptional mechanical and tribological properties. This study investigates the fabrication of Titanium–Graphene Nanoplatelets (Ti-GNPs) coatings using Cold Gas Spray (CS), a technique that preserves material integrity by avoiding high-temperature degradation. Multilayer GNPs (0.5 wt%) were incorporated into Grade 1 Ti powder, followed by Heat Treatments (HT) at 700 °C and 1000 °C to enhance cohesion within the composite. Mechanical and tribological tests revealed significant enhancements in the Ti-GNPs coatings. The HT at 1000 °C increased tensile strength to 539.45 MPa and hardness to 264 HV, achieving 28% improvement compared to pure Ti. Wear tests demonstrated a 25% reduction in friction coefficient, attributed to the lubricating effect of GNPs. Microstructural analysis confirmed the successful integration of GNPs with minimal degradation, though Raman spectroscopy indicated minor structural defects at higher temperatures. These findings demonstrate that Ti-GNPs coatings provide superior mechanical performance and wear resistance, offering potential for industrial applications in extreme environments.

1. Introduction

Nano-platelets Graphene (GNPs) represent a promising advancement in the development of advanced materials due to their exceptional chemical, mechanical, and tribological properties [1,2]. Their high strength, flexibility, and conductivity make them suitable as reinforcements in various matrices, particularly in metals. Titanium (Ti), widely used in the aerospace, biomedical, and automotive industries for its low density, high strength, and excellent corrosion resistance, faces limitations in wear resistance, electrical conductivity, and durability under extreme conditions [3–6]. To address these challenges, the incorporation of GNPs into Ti matrices has emerged as a solution to enhance both mechanical and functional properties, such as improved tribological performance and charge transfer [7,8].

The ability of GNPs to act as effective reinforcements lies in their large specific surface area and superior stress-transfer capacity, which significantly enhance the properties of composite materials [9]. However, integrating GNPs into metallic matrices poses challenges. Two critical issues are the homogeneous dispersion of GNPs within the matrix and achieving robust adhesion at the metal–graphene interface [10–13]. These factors are key to maximizing the potential benefits

of GNPs as reinforcements. Various techniques have been explored for incorporating GNPs into metal matrices, such as Spark Plasma Sintering (SPS), High-Velocity Oxygen Fuel (HVOF) spraying, and laser deposition [14,15]. While these methods have shown some success in improving the properties of composites, they often face limitations, including thermal degradation of GNPs during processing and insufficient control over their dispersion and adhesion within the matrix [16].

Despite advancements in GNPs-reinforced composite, achieving efficient integration remains challenging. For instance, uniform dispersion of GNPs and the formation of strong metal–graphene interfaces are often hindered by the tendency of GNPs to agglomerate and by limited chemical interactions with the matrix [10,17,18]. Addressing these challenges is critical to unlocking the full potential of these composite materials in industrial applications, particularly in sectors requiring enhanced wear resistance and structural reliability.

The use of CS offers significant advantages over other techniques, as it facilitates the incorporation of GNPs into Ti coatings without compromising their structural integrity. Unlike HVOF or Selective Laser Melting (SLM), CS minimizes the risks of thermal degradation while

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Glossary

σ_u	Ultimate Tensile Strength
σ_y	Yield Stress
ϵ	Deformation
E	Elastic Modulus
CoF	Friction Coefficient
CS	Cold Gas Spray
FWHM	Full Width at Half Maximum
GFs	Carbon Nanofibers
GNPs	Nano-platelets Graphene
GR	Graphene
HT	Heat Treatments
HVOF	High-Velocity Oxygen Fuel
LS	Laser Scattering
Ra	Arithmetic Average Roughness
SEM	Scanning Electron Microscopy
SLM	Selective Laser Melting
SPS	Spark Plasma Sintering
TEM	Transmission Electron Microscopy
Ti-GNPs	Titanium–Graphene Nanoplatelets
XRD	X-ray Diffractometry

ensuring sufficient particle adhesion and uniform distribution within the matrix [19]. Furthermore, the flexibility of this technique allows for the integration of post-deposition HT, which can further enhance microstructural cohesion and optimize the metal–graphene interface [20, 21]. By avoiding the high temperatures required in conventional processes, CS preserves the intrinsic properties of both the Ti matrix and GNPs, reducing oxidation and thermal degradation risks [22,23]. Additionally, the high kinetic energy involved in CS deposition promotes the formation of dense coatings with strong interfacial adhesion [24].

The primary aim of this study is to investigate the mechanical, tribological, and microstructural properties of Ti coatings reinforced with GNPs, fabricated via CS. By analyzing the effects of GNPs incorporation and post-deposition HT at 700 °C and 1000 °C, this work seeks to determine how these treatments influence the dispersion of the GNPs, the adhesion at the Ti-GNPs interface, and the overall performance of the composite coatings.

To this end, the study hypothesizes that GNPs reinforcements significantly enhances the tensile strength, hardness, wear resistance, and thermal stability of Ti coatings compared to pure Ti. Furthermore, HT is expected to improve the microstructural cohesion and promote a robust interface between Ti and GNPs, enabling the development of coatings with superior properties. By addressing the current challenges in fabricating GNPs-reinforced coatings, this research aims to provide insights into optimizing CS processes for industrial applications requiring materials with exceptional performance.

2. Materials and methods

2.1. Materials

In this study, multilayer GNPs were used as the reinforcing material, and Grade 1 Ti powder served as the metallic matrix. The GNPs, supplied by Nanografi Technology (Çankaya, Turkey), feature 99.9% purity, an average thickness of 5 nm, a surface area of 170 m²/g, and an average lateral diameter of 30 µm. This material was received in its as-received state without undergoing additional treatments before characterization and mixing. The water-atomized irregularly shaped Ti powder was supplied by CNPC (Shanghai, China), with an average

particle size of 45 µm and a purity of 99.9%, O 0.2% Max. Both materials were selected for their complementary mechanical properties.

The characterization of the Ti powder was conducted to assess its morphology, flowability, and crystalline structure. To determine the particle size distribution, the Laser Scattering (LS) technique was employed using the LS13320 equipment (Beckman Coulter, Brea, CA, USA), in accordance with ASTM B822-02 [25]. The flowability of the powder was measured using a Hall Flowmeter Funnel with a 2.5 mm diameter orifice and a 50 g capacity, following ASTM B213-20 [26]. The morphology of the Ti powder was evaluated by Scanning Electron Microscopy (SEM) using a Phenom ProX G6 (Thermo Scientific, Eindhoven, Netherlands), operating at 15 kV and a magnification of 1000x to observe the powder's morphology.

For the microstructural analysis, X-ray Diffractometry (XRD) was performed using a PANalytical X'Pert PRO MPD alpha1 powder diffractometer (PANalytical, Malvern, UK) in Bragg–Brentano $\theta/2\theta$ geometry. Cu K α radiation with a wavelength of 1.5418 Å was used, operating at 45 kV and 40 mA. The scanning range was from 4.5° to 100° in 2θ , with a step size of 0.026° and a measurement time of 100 s per step. The average crystallite size was determined from the broadening of the diffraction peaks using the Rietveld method. Additionally, potential defects and impurities in the Ti crystal structure were evaluated.

The GNPs powder was characterized by Raman spectroscopy using the LabRam HR 800 system (Jobin-Yvon, Longjumeau, France), employing a 532 nm laser to identify the D (~1350 cm⁻¹), G (~1580 cm⁻¹), and 2D (~2700 cm⁻¹) bands. The measurements were coupled with a BXFM optical microscope (Olympus, Tokyo, Japan) to enhance spatial precision, detecting a low level of defects in the GNPs. In addition, Transmission Electron Microscopy (TEM) was performed using 1010 (Jeol, Tokyo, Japan) equipped with an Orius CCD camera (Gatan, Walnut Creek, CA, USA) to observe interplanar spacing and the number of Graphene (GR) layers. Finally, the surface distribution and lateral morphology of the GNPs were evaluated by high-resolution scanning electron microscopy (HR-SEM) using a JSM-7001F system (Jeol, Tokyo, Japan), operating at 10 kV and employing secondary and backscattered electron detectors to identify possible agglomerations and defects.

2.2. Composites fabrication

The Ti powder reinforced with GNPs (Ti-GNPs) 0.5 wt% was prepared by dispersing 5 g of GNPs in 2000 ml of ethanol using sonication. An ultrasonic equipment JP Selecta (Albera, Barcelona, Spain), operating at 360 W and 40 kHz for 60 min. This process ensured a homogeneous dispersion of the nanoplatelets in the solvent.

Subsequently, 1000 g of Ti powder was added to the GNPs suspension. The mixture was stirred with a mechanical stirrer F20100152 (Velp, Usmate, Italy) at 500 rpm for 30 min, ensuring a uniform distribution of the nanoplatelets in the Ti powder. The suspension was then filtered using a 10 µm filter paper, and the retained material was dried in a UFE400 oven (MEMMERT, Büchenbach, Germany) at 60 °C for 4 h to completely remove the ethanol.

Finally, the dry material was subjected to planetary milling in a PM 400 planetary mill (RETSCH, Haan, Germany), using 1.0 mm diameter balls ZnO₂ with a weight ratio of 1:2 (material-balls). The milling was carried out at 200 rpm for 90 min. This process was conducted in an argon atmosphere to prevent oxidation of the material. No control agent was used during this process.

2.3. Cold gas spraying deposition

The Ti and Ti-GNPs coatings were deposited using the CS technique, utilizing a PCS100 system (Plasma Giken, Saitama, Japan). Nitrogen was employed as an inert propellant gas for the deposition, with a purity of 99.99%, maintaining a gas temperature of 1000 °C and a pressure of 6.0 MPa throughout the entire process. The grade 2 Ti sheets used as the substrate were pre-treated through a blasting process

Table 1
Sample nomenclature.

Nomenclature	Description
Ti powder	Grade 1 Ti powder in its original state, as supplied by the manufacturer.
Ti (Coating)	Ti coating in As sprayed state, deposited by CS, without thermal treatment.
Ti HT 700 °C (Coating)	Ti coating thermally treated at 700 °C.
Ti HT 1000 °C (Coating)	Ti coating thermally treated at 1000 °C.
Ti-GNPs powder	Ti powder composite reinforced with GNPs.
Ti-GNPs (Coating)	Coating deposited with Ti-GNPs powder in As sprayed state.
Ti-GNPs HT 700 °C (Coating)	Ti-GNPs coating thermally treated at 700 °C.
Ti-GNPs HT 1000 °C (Coating)	Ti-GNPs coating thermally treated at 1000 °C.

with Al_2O_3 to improve coating adhesion. This process allowed for an Arithmetic Average Roughness (Ra) $> 7.5 \pm 0.5 \mu\text{m}$, according to the ASTM-D4417 and ISO-8501-1 standards [27,28].

Two types of coatings were prepared: one composed solely of “as-received” Ti, and another of Ti-GNPs at a concentration of 0.5% wt. During deposition, the Ti and Ti-GNPs particles were accelerated toward the substrates at a standoff distance of 30 mm, controlled by a robotic arm. The robot operated at a travel speed of 500 mm/s, making a traditional path and passes with an increment of 1.0 mm per sweep. The powder feed rate was set at 0.74 g/s, ensuring a uniform distribution of the projected material. After deposition, the coatings were allowed to cool to room temperature.

2.4. Post-treatment

The deposited coatings were subjected to two sequential HT in a GHA 12/450 tubular furnace (Carbolite, Hope, UK) to enhance material cohesion and promote interaction between the GNPs and the Ti matrix. Both treatments were carried out under a controlled argon atmosphere (99.99% purity) and vacuum ($\sim 10^{-2}$ mbar), which prevented oxidation of the coatings.

The first HT was conducted at 700 °C, with a constant heating rate of 10 °C/min, and the samples were held at this temperature for 3 h. This HT was designed to induce initial modifications in the microstructure, ensuring that the GNPs retained their integrity. The cooling process was performed in a controlled manner over 12 h to avoid the formation of thermal stresses in the coatings. The second HT was carried out at 1000 °C, under the same heating conditions and hold time, with the aim of increasing atomic diffusion in the Ti matrix, which promoted interaction and cohesion between the GNPs and the metallic matrix. As with the previous treatment, gradual cooling over 12 h minimized the risk of defects in the coating structure.

2.5. Sample designation

Table 1 specifies the nomenclature used for the samples analyzed throughout this study, in order to facilitate their identification and tracking of the presented results.

2.6. Microstructure characterization

The microstructural characterization of the Ti-GNPs coatings was carried out using microscopy and diffraction techniques to assess the distribution of GNPs reinforcement and the microstructural integrity of the Ti matrix after the CS deposition process. The cross-sectional samples of the coatings were prepared following standard metallographic procedures in accordance with ASTM E1920-03 standard [29], which includes cutting, mounting, and polishing of the cross-sections. The average porosity of the Ti and Ti-GNPs coatings was quantified through grayscale image analysis at 200x magnification. A thresholding method was applied to distinguish porous areas in each image, calculating the porosity percentage as the average from ten images per sample. This procedure was conducted in accordance with Test Method B of ASTM E2109-14, providing a representative value for the average porosity [30].

The observation of the cross-sections was performed using a JSM-7001F high-resolution SEM to obtain detailed images of the GNPs distribution within the Ti matrix. Additionally, a cross-section of samples subjected to bending fracture until failure was analyzed, observing the fractured surface of a fractured deposit to evaluate the adhesion and distribution of the GNPs to the Ti particles. The microstructural analysis was complemented by XRD using an X'Pert PRO MPD to identify possible alterations in the crystalline structure of Ti after CS deposition. A comparative analysis was conducted between the coated samples and the original (“as-received”) Ti powder. Measurements included the analysis of the Full Width at Half Maximum (FWHM) of the diffraction peaks to evaluate changes in crystallite size and the presence of microstrains or residual stresses induced during the process. The diffraction patterns were refined using the Rietveld method to obtain precise information on the crystal structure.

Additionally, Raman spectroscopy was performed using a LabRam HR 800 to evaluate the microstructural integrity of the Ti-GNPs after the deposition process, comparing the characteristic G, D, and 2D bands of GR that were identified. This provided information regarding the presence of defects and the preservation of the crystalline order of the GNPs during and after the CS process.

2.7. Mechanical characterization

The mechanical characterization of the coatings was carried out through microhardness, tensile, and wear tests, in order to evaluate the material's resistance to deformation and its tribological response. Vickers microhardness was measured on the cross-sections of the coatings using an HMV microhardness tester (Shimadzu, Tokyo, Japan), applying a 200 g load for 15 s. Ten indentations were uniformly distributed on each sample, and the average hardness values were calculated according to ASTM E384-99 [31]. This analysis allowed a comparison of hardness properties between the pure Ti coating and the coatings reinforced with GNPs and those HT, providing information about the influence of reinforcement on local deformation resistance.

Additionally, tensile tests were performed according to ASTM E8/E8M [32], using flat sample fabricated from the deposited coatings. The tests were conducted on an Instron 3366 universal testing machine (Norwood, MA, USA), equipped with a 10 kN load cell and an axial extensometer. The test speed was set to 0.2 mm/min, and the data were recorded using the Bluehill Universal software, in compliance with ASTM E83 and ISO 9513 standards [33,34]. The stress-strain curves obtained allowed for the determination of key properties such as maximum tensile strength and Young's modulus, comparing the pure Ti coatings with the Ti-GNPs coatings.

Finally, to evaluate wear resistance, the “Ball-on-Disk” sliding technique was implemented in accordance with ASTM G99-04 [35]. The equipment used was manufactured by CM4 Ingenierya SL (Cervelló, Spain). The samples were prepared to achieve a maximum surface roughness Ra de $0.8 \mu\text{m}$. The test was performed at a constant temperature of 23 ± 2 °C and a relative humidity of $50 \pm 5\%$, applying a vertical load of 10 N on a WC-Co ball with a 10 mm diameter, which slid over the coating surface without lubrication, following a circular track with a diameter of 14 mm. A total of 22,733 cycles were performed, covering a total distance of one kilometer to ensure wear stability.

was reached. The results of the continuous monitoring of the Friction Coefficient (CoF) were graphically represented, and the average from the final 7000 cycles of the stabilization zone was estimated. The wear rate was calculated according to the procedure established in ASTM G99-04 [35], by measuring the wear tracks, which were observed and characterized using SEM. Three replicates of each test were performed to ensure the repeatability of the results, and the average wear rate and CoF values were statistically analyzed to validate data consistency.

3. Results and discussion

3.1. Characterization of the powders

The morphological analysis of Ti powder, presented in Fig. 1, reveals an irregular morphology, characteristic of the water atomization process. This type of morphology is commonly attributed to the rapid and asymmetric solidification of the metallic material when interacting with the aqueous medium during atomization. These results suggest that the irregular morphology may influence the powder's behavior during deposition by CS, due to possible variations in the particle velocity distribution, which aligns with previous studies on the influence of morphology on the performance of metallic powders in CS. In Fig. 5, the XRD of the Ti powder reveals a hexagonal close-packed (HCP) crystalline structure, typical of the Ti α phase. The eight main identified peaks, especially the most prominent peak corresponding to the (101) plane at 40.171° , confirm the predominance of this phase. These findings are consistent with the expected structure for pure Ti powders and suggest favorable crystalline stability for deposition processes without compromising the material's integrity [36,37].

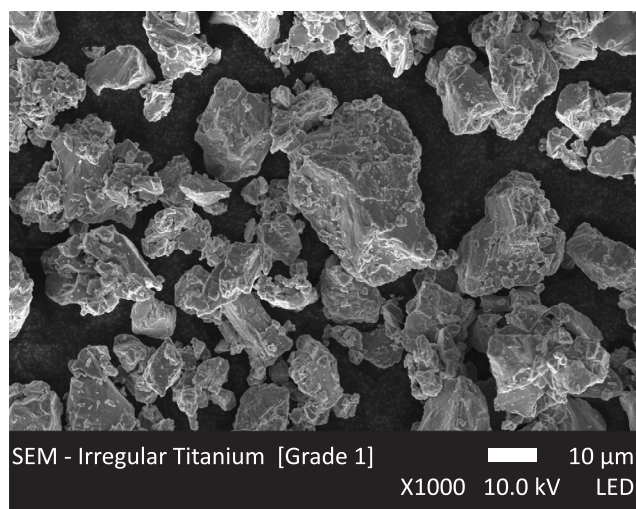


Fig. 1. Characterization of the Ti powder.

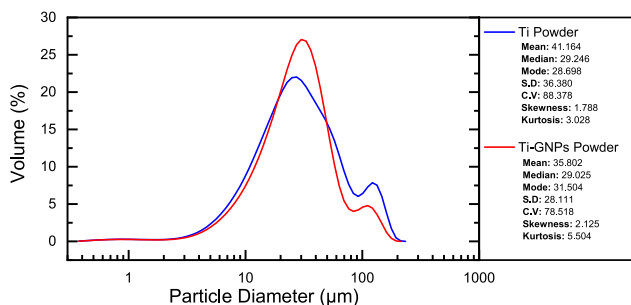


Fig. 2. LS of the Ti powder.

Regarding crystallite size, Rietveld refinement revealed an average value of 528 nm as shown in Table 2. This size is indicative of a refined microstructure that could contribute to higher densification of the material during the consolidation process. The low microstrain observed (0.00044) suggests an absence of significant residual stresses in the material in its initial state, which is a key factor in minimizing defects during CS deposition and ensuring greater cohesion between the particles in the final coating.

The particle size analysis of Ti powder using LS, illustrated in Fig. 2, shows a broad distribution, with an average size of $41.16 \mu\text{m}$ and values D10, D50, D90 of 10.03, 29.25, $93.41 \mu\text{m}$, respectively. The significant size dispersion is reflected in a standard deviation of $36.38 \mu\text{m}$ and a coefficient of variation of 88.38%. The distribution exhibits positive skewness (1.79), indicating the presence of particles larger than the average. Most of the particles fall within the optimal size range for deposition by CS, which could facilitate achieving the critical velocity required for proper particle adhesion. This behavior is consistent with observations by Schmidt et al. in similar powders, suggesting that Ti powder is suitable for use in high-velocity impact processes [37].

3.2. Characterization of graphene nanoplatelets

The images obtained by SEM in Fig. 3 reveal nanoplatelets with irregular morphologies and lateral sizes ranging from $3 \sim 40 \mu\text{m}$. Additionally, agglomerations in multilayer structures are observed, suggesting the presence of interlayer interactions, likely due to van der Waals forces. The TEM analysis Fig. 3 provided a more detailed view of the internal structure of the GNPs. At higher magnification, the atomic planes of GR were identified, confirming the typical crystalline arrangement of carbon layers in the material.

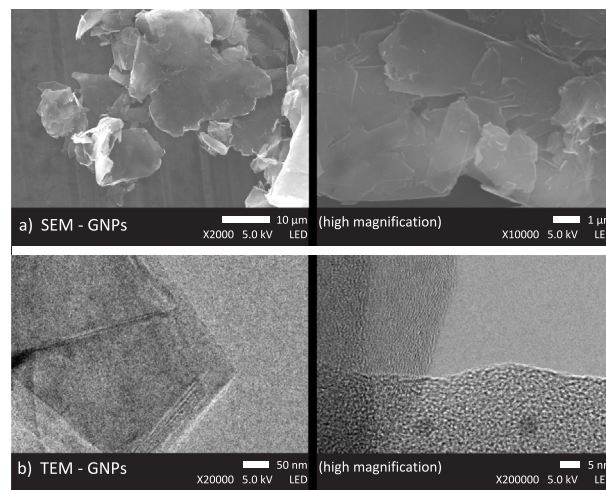


Fig. 3. SEM and TEM images of GNPs.

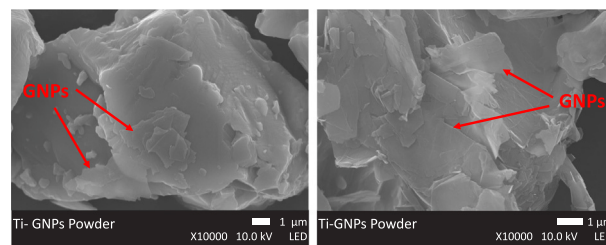


Fig. 4. SEM images of Ti-GNPs powder.

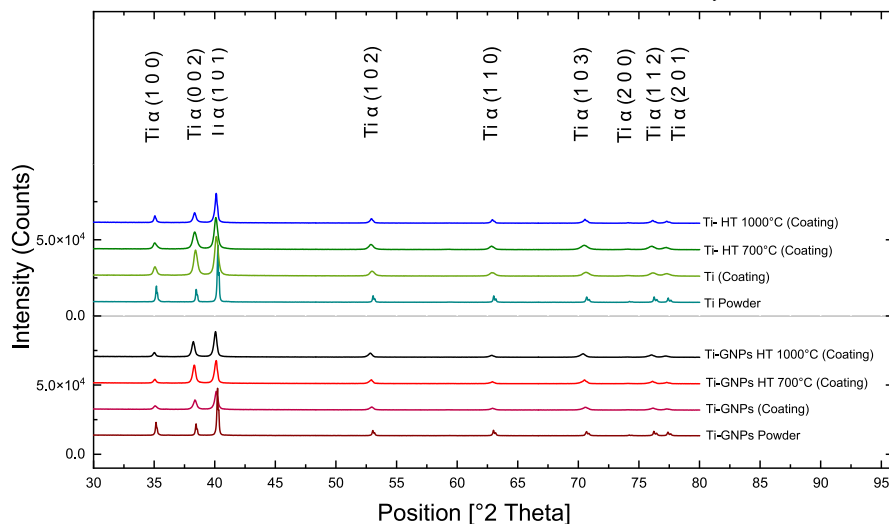


Fig. 5. XRD pattern.

Moreover, Raman spectroscopy Fig. 6 showed the spectrum with the characteristic peaks of GR, providing insights into its two-dimensional crystalline structure. Unlike three dimensional crystalline materials, which exhibit distinct peaks in XRD patterns due to their periodicity in all directions, graphene's order is confined to two dimensions. This bidimensionality results in the absence of strong, well-defined XRD peaks, particularly for disordered nanoplatelets. The Raman spectrum, with a prominent G band at 1580 cm^{-1} and a 2D band at 2700 cm^{-1} , is more suitable for analyzing the structure of GR. The $I(2D)/I(G)$ ratio of less than 1 confirms the presence of multilayer GR, while the negligible D band at 1350 cm^{-1} was observed, indicating a low level of defects in the nanoplatelets and, therefore, high material purity. [38,39]

3.3. Characterization of Ti-GNPs reinforced powder

Fig. 4 shows SEM images of Ti powder mixed with Ti-GNPs at 0.5 wt%, after the low-energy planetary milling process. A mixture with a loose dispersion of GNPs can be observed, where the nanoplatelets are not fully adhered to the surface of the Ti particles. Although some particles show adhesion of the Ti-GNPs, areas can be identified where the nanoplatelets are decoupled from the Ti matrix and dispersed throughout the mixture, with signs of agglomeration in certain regions.

In Fig. 2, the particle size distribution of Ti-GNPs powder is shown, where a significant decrease in the size of the larger particles can be observed, reflected by the reduction of the D90 value from $93.41 \mu\text{m}$ to $65.67 \mu\text{m}$, indicating effective fragmentation of the larger particles. This change is also accompanied by greater uniformity in particle

distribution, as evidenced by the reduction in standard deviation from $36.38 \mu\text{m}$ to $28.11 \mu\text{m}$ and in the coefficient of variation from 88.38% to 78.52%. Additionally, the increase in *skewness*, from 1.79 to 2.13, and in *kurtosis*, from 3.03 to 5.50, suggests a higher concentration of small particles and a more homogeneous distribution. These changes imply that the milling process improved the powder's uniformity without generating an excess of fine particles, which is favorable for the CS process, as it requires controlled particle size and greater material homogeneity.

XRD patterns shown in Fig. 5 confirm that the crystalline structure of Ti has not undergone significant alterations after the incorporation of GNPs and milling. Despite the reinforcement and mechanical treatment, no deviations are observed in the characteristic peaks of Ti, indicating that the crystalline structure remained unchanged. No additional peaks or variations in the width of the existing peaks were detected, suggesting that no significant deformations occurred in the Ti crystal lattice. Furthermore, the absence of secondary peaks confirms that no contaminants or residues from the milling balls were introduced during the process. This indicates that the low energy used during milling was effective in preserving the material's purity.

The Raman spectroscopy analysis, as shown in Fig. 6, confirms the presence of GNPs in the Ti-GNPs reinforced powder. The characteristic peaks in the G and 2D bands were clearly identified. The absence of the D band, approximately at (1350 cm^{-1}) , confirms that the GR did not suffer any alterations or defects in its crystalline structure after the mixing and planetary milling process.

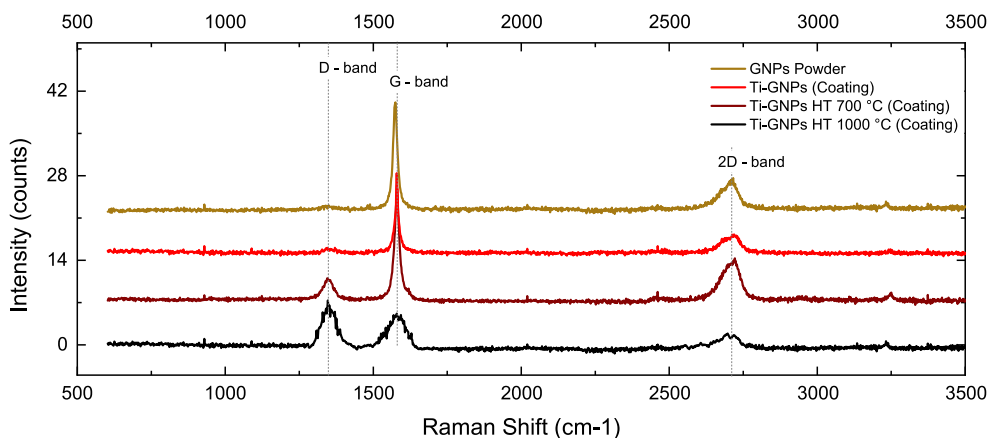


Fig. 6. Raman spectra.

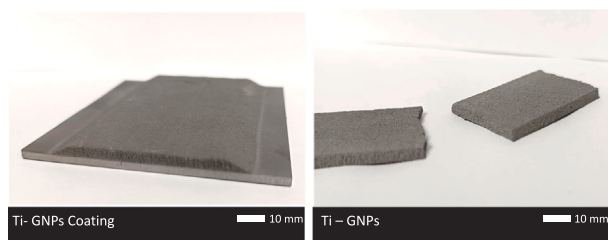


Fig. 7. Images Ti-GNPs coating for CS.

3.4. Characterization of the coatings

In Fig. 7, the coatings of Ti and Ti-GNPs with 0.5 wt% deposited by CS under the same projection conditions are shown. Both exhibited good cohesion, with no cracking, and an average porosity of $1.5 \pm 0.10\%$. This porosity value is consistent with those reported in previous studies on Ti coatings deposited by CS [36,40]. Additionally, no significant differences were observed in deposition efficiency, nor in the growth of thickness and surface roughness, indicating that the incorporation of 0.5 wt% GNPs into the Ti matrix does not affect the process performance or particle adhesion.

3.5. Microstructural properties

In Fig. 8, the microstructural characterization of Ti and Ti-GNPs coatings is presented, in both the “as-sprayed” condition and after being subjected to HT at 700 and 1000 °C. The overall porosity is less than 1.5%. The addition of GNPs does not significantly affect the density of the Ti matrix. This suggests that the compactness of the coating remains stable with or without reinforcement. In the “as-sprayed” state, the impacted particles show notable deformations, and well-defined boundaries between them are observed. However, as the HT temperature increases, a progressive reduction of the boundaries between the particles is observed, which is attributed to an atomic diffusion process. This phenomenon, enhanced by the energy accumulated during the CS process, leads to a homogeneous microstructure with uniformly distributed equiaxed grains after HT at 1000 °C.

The HT also significantly affects the recrystallization process of the coatings. In Fig. 8 in the “as-sprayed” state, the microstructure shows a high density of dislocations and deformations, a result of cold hardening caused by particle impact. At temperatures of 700 and 1000 °C, these dislocations act as preferential sites for the nucleation of new grains. The recrystallization process, driven by atomic diffusion and the reduction of the material’s internal energy, favors the formation of smaller and equiaxed grains, replacing the previous interparticle boundaries. This improves the cohesion of the matrix and homogeneously redistributes the GNPs, contributing to microstructural stability. At higher temperatures, the carbon from the GNPs can interact with the Ti matrix, forming small amounts of TiC, which, although not detectable by XRD, increase the coating’s hardness and strength by providing additional reinforcement points.

The XRD results, presented in Fig. 5, reveal a significant evolution in crystallite size and microstrain of the Ti coating after HT at 1000 °C. In the Ti Coating, the crystallite size is 39.7 nm with a microstrain of 0.002, as shown in Table 2, reflecting a microstructure typical of CS deposition. After HT at 1000 °C, the crystallite size increases markedly to 51.8 nm, while the microstrain decreases to 0.00086. This behavior suggests a recrystallization process, with the release of internal stresses and the reduction of defects, resulting in a more stable microstructure. The increase in crystallite size and reduction in microstrain suggest improved cohesion and uniformity of the coating, crucial for optimizing its mechanical properties and long-term resistance.

SEM images of the cross-section Fig. 9 together with the Raman spectra in Fig. 6 provide a comprehensive view of the microstructural states and changes in the Ti-GNPs coatings. In Fig. 9a, the presence of GNPs is observed after the projection process, displaying a heterogeneous distribution within the titanium matrix. These nanoplatelets are partially embedded in the deformed surfaces and interstices of the Ti particles, suggesting mechanical anchoring during deposition. However, localized agglomerations of GNPs are also identified, which can be attributed to their inherent nature and the van der Waals interlayer interactions that tend to promote agglomeration. Raman spectroscopy (Fig. 6, Ti-GNPs Coating spectrum curve) supports the preservation of the graphene’s crystalline structure after deposition, as the characteristic peaks of the G and 2D bands show no significant changes. This confirms that the CS process does not compromise the structural integrity of graphene.

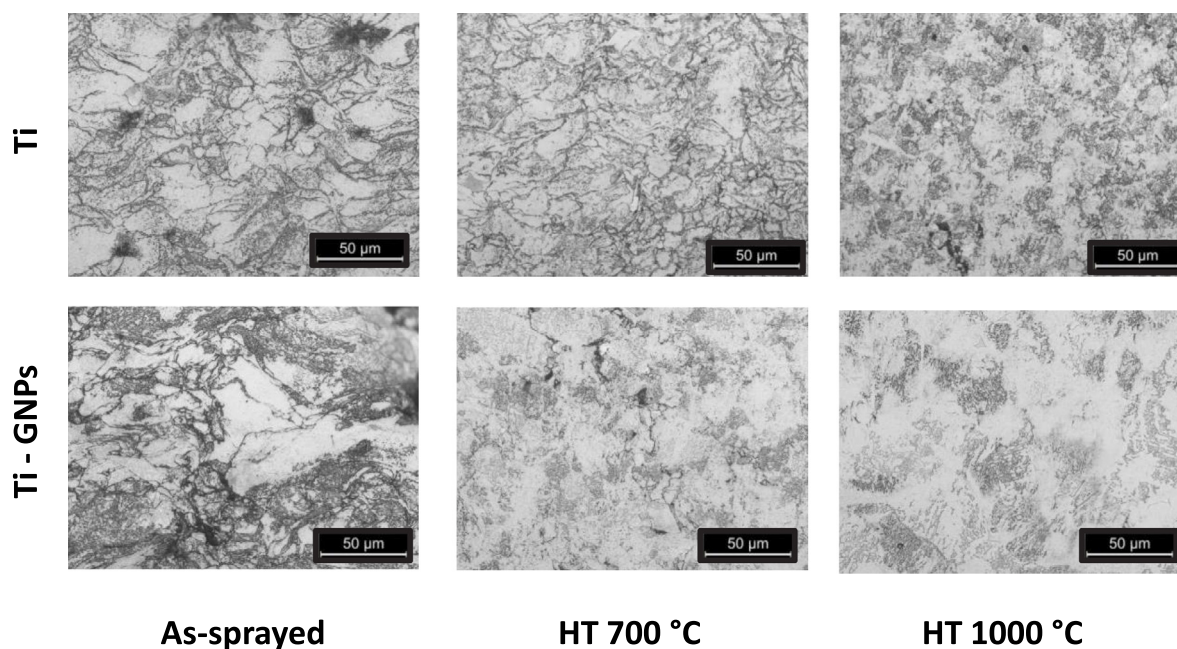


Fig. 8. Images of microstructure.

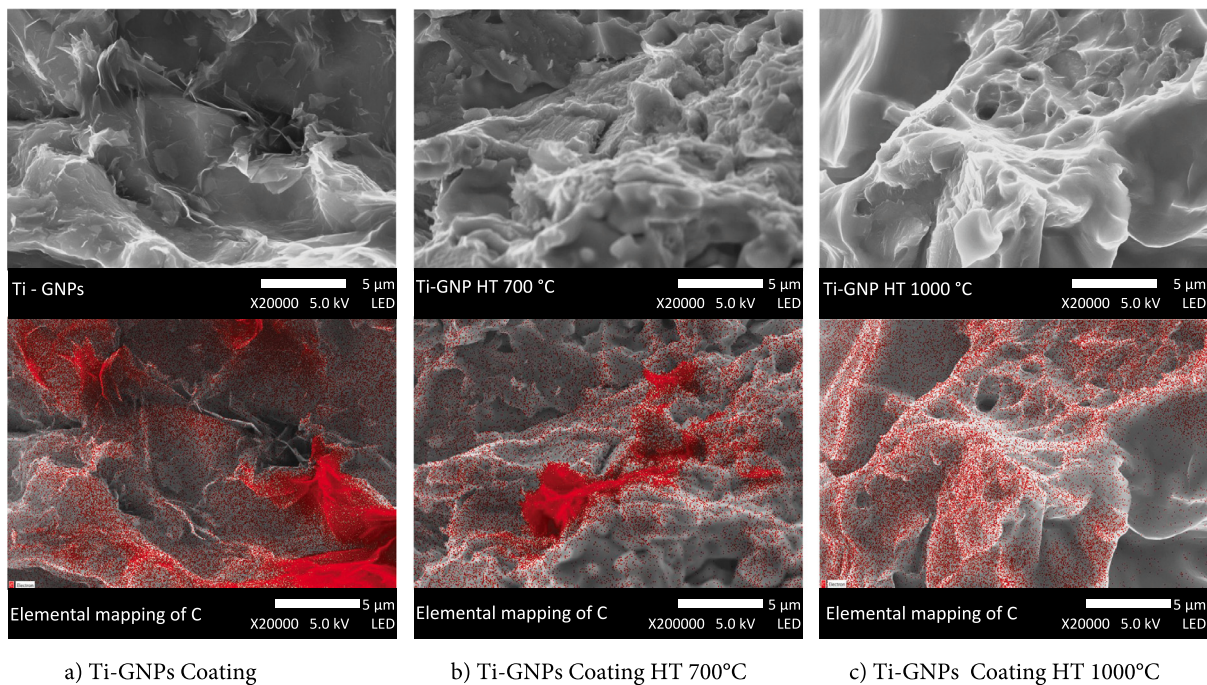


Fig. 9. SEM cross section of CS Ti-GNPs coatings.

After the HT at 700 °C, SEM images Fig. 9 reveal slight modifications in the morphology of the nanoplatelets, likely due to surface interactions between the carbon from the GNPs and the Ti matrix. This phenomenon is consistent with the observed increase in the intensity of the D-band in the Raman analysis (Fig. 6, Ti-GNPs Coating HT 700 °C spectrum curve), suggesting the appearance of structural defects in the GNPs. However, these defects are not sufficient to induce a phase change or the formation of significant compounds, such as titanium carbide (TiC), which would indicate carbon diffusion into the matrix. This is corroborated by XRD analysis Fig. 5, where no characteristic TiC peaks are detected, indicating that carbon diffusion into the matrix is limited and does not result in the detectable formation of this compound.

While the applied thermal energy does not lead to chemical transformation, it does enhance the physical adhesion between the GNPs and the Ti particles due to increased atomic mobility and van der Waals forces. Furthermore, the increase in the titanium's surface energy promotes the adaptation of graphene nanoplatelets to surface irregularities in the matrix, improving their integration without significantly compromising their crystalline structure [8,41,42].

In the Ti-GNPs coating treated at 1000 °C, SEM analysis Fig. 9 reveals the apparent visual absence of GNPs within the titanium matrix; they have transitioned from distinguishable phases to a more integrated state within the matrix, contributing to improved interfacial adhesion. This phenomenon is attributed to their integration into the matrix, resulting from synergistic microstructural transformations occurring at

high temperatures, including sintering, recrystallization, and atomic diffusion processes. The HT at 1000 °C induces a densification process characterized by the elimination of interparticle boundaries and the incorporation of GNPs into the Ti matrix. These changes produce a more uniform and cohesive structure, with reduced porosity and the formation of equiaxed grains that enhance the overall integrity of the matrix. Unexpectedly, the crystallite size decreases to 50.5 nm, a behavior indicative of a dynamic recrystallization mechanism. This process replaces larger, stressed grains with finer, defect-free grains, improving the mechanical stability and load distribution of the material. The recorded microstrain of 0.001640 suggests that, although internal stresses have been partially relaxed through diffusion mechanisms, residual stresses remain localized at the interface between GNPs and the Ti matrix. These stresses likely arise from lattice mismatches and limited chemical interactions at elevated temperatures.

Raman spectroscopy analysis (Fig. 6, Ti-GNPs Coating HT 1000 °C spectrum curve) confirms the presence of graphene structures, providing further details on the effects of HT, showing an increase in the D-band intensity, indicative of new structural defects in the GNPs. These defects include vacancies, lattice distortions, and interlayer disruptions resulting from carbon diffusion into the Ti matrix at high temperatures. This diffusion leads to the formation of titanium carbide (TiC) at the interface, which is not detectable via XRD due to its low volume fraction. This phenomenon, widely documented in studies on titanium–carbon compounds, underscores the importance of Ti-C interactions. As a hard and stable phase, TiC provides reinforcement

Table 2
Rietveld refinement results of Ti coating.

Material	RwP %	Goff	D, Crystallite size nm	e, microstrain rms	a Å	c Å
Ti powder	10.5	2.5	198	0.000137	3.42678	5.44228
Ti (Coating)	9.8	1.8	39.7	0.002000	3.43196	5.44172
Ti HT 700 °C (Coating)	7.5	2.3	53.1	0.001830	3.44650	5.45167
Ti HT 1000 °C (Coating)	9.1	2.3	51.8	0.000860	3.42935	5.44774
Ti-GNPs powder	8.9	2.1	170	0.000100	3.42695	5.44196
Ti-GNPs (Coating)	7.9	2.1	77.3	0.001700	3.43603	5.46750
Ti-GNPs HT 700 °C (Coating)	7.8	2.1	76.0	0.001500	3.43138	5.45314
Ti-GNPs HT 1000 °C (Coating)	7.2	1.9	50.5	0.001640	3.43370	5.46250

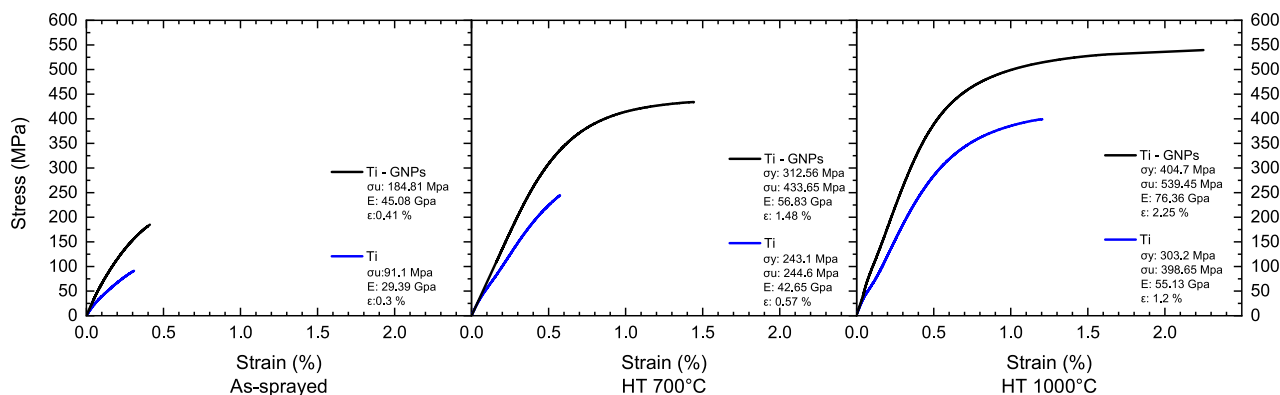


Fig. 10. Tensile test results.

points that significantly improve the coating's hardness and mechanical strength. The coexistence of the D and G bands in the Raman spectrum confirms that graphene structures persist within the matrix, suggesting their role in maintaining reinforcement functionality and facilitating stress transfer [43–45].

3.6. Hardness analysis

Ti coatings show a progressive increase in hardness as HT are applied. In the “As-sprayed” state, the hardness is 174 ± 18 HV, which is consistent with other studies on impact-induced hardening during the CS process [40]. The HT at 700 °C raises the hardness to 201 ± 12 HV, a 15% increase, which is primarily attributed to the reduction of internal stresses and the onset of recrystallization. Finally, the HT at 1000 °C increases the hardness to 224 ± 12 HV, a 28% increase compared to the “As-sprayed” state [46,47].

For Ti coatings Ti-GNPs, the initial hardness is 189 ± 10 HV, increasing to 207 ± 15 HV after the 700 °C HT and to 264 ± 15 HV after the 1000 °C HT. These results indicate that the addition of GR improves hardness under all conditions and that the HT at 1000 °C maximizes this improvement, especially in Ti-GNPs coatings, which can be attributed to a fine dispersed TiC precipitates especially in the periphery of the Ti particles due to the diffusion of C from the GNPs to the Ti matrix.

3.7. Tensile test

The results obtained from the tensile tests are presented in Fig. 10. They reveal a significant improvement in the mechanical properties of Ti coatings by incorporating GNPs and subjecting the material to HT at different temperatures. The as-sprayed Ti-GNPs coating showed an increase in Ultimate Tensile Strength (σ_u) of 184.81 MPa, compared to pure Ti which presented a value of 91.10 MPa. This increase is accompanied by a rise in the Elastic Modulus (E) from 29.39 GPa in pure Ti to 45.08 GPa in Ti-GNPs, suggesting that the GNPs act as an effective reinforcement, enhancing the stiffness of the material. Furthermore, a slight improvement was observed in the maximum strain capacity Deformation (ϵ), increasing from 0.3% in pure Ti to 0.41% in Ti-GNPs.

The HT at 700 °C resulted in a considerable improvement in the properties of the Ti-GNPs composite, raising the σ_u to 433.65 MPa and the Yield Stress (σ_y) to 312.56 MPa, compared to pure Ti treated at the same temperature, which showed values of 244.60 MPa and 243.10 MPa, respectively. Similarly, the E of the treated Ti-GNPs was 56.83 GPa, while pure Ti reached only 42.65 GPa. Moreover, the maximum strain ϵ of the Ti-GNPs composite was 1.48%, representing a significant increase in ductility compared to Ti 0.57%, highlighting the ability of HT to improve the interaction between the GNPs and

the Ti particle, thereby optimizing the microstructural cohesion of the coating.

Finally, the HT at 1000 °C exhibited the highest improvements in the mechanical properties of the Ti-GNPs coating, reaching an σ_u of 539.45 MPa, a σ_y of 404.70 MPa, and an E of 76.36 GPa, significantly surpassing the values of pure Ti treated at the same temperature, which reached 398.65 MPa, 303.20 MPa, and 55.13 GPa, respectively. The maximum strain of the Ti-GNPs treated at 1000 °C was 2.25%, indicating a remarkable improvement in ductility and the capacity for deformation without fracture.

These results highlight the importance of high-temperature HT in optimizing Ti-GNPs coatings. The atomic diffusion and recrystallization processes promoted by the HT play a crucial role in improving the material's microstructure, as previously discussed. Specifically, the diffusion of carbon from the GNPs into the Ti matrix facilitates the formation of TiC at the Ti-GR interfaces. This compound acts as an effective reinforcement that enhances the mechanical strength of the coating. However, the Raman spectrum reveals structural modifications in the Carbon Nanofibers (GFs), indicating defects induced by high temperatures, reflecting a balance between structural degradation and the generation of reinforcements. Despite these modifications, elevated temperatures are beneficial in creating additional reinforcement points that optimize load transfer and redistribute stresses within the matrix. This network of reinforcements not only improves the material's ability to withstand applied loads but also limits defect propagation in the microstructure, contributing to greater ductility and strength of the coating under stress conditions [8,41,42].

3.8. Ball on disk test

In Fig. 11, the results of the evolution of CoF with the testing time are presented. The inclusion of GNPs in the Ti matrix shows a significant improvement in the tribological behavior of the coatings. While the Ti coating CoF of 0.94 ± 0.030 exhibits a relatively high coefficient, the addition of GNPs reduces this value to 0.86 ± 0.045 , achieving a reduction in the CoF of approximately 8.5% compared to pure Ti. This effect is attributed to the intrinsic lubricating effect of GNPs [7,48]. This effect is even more pronounced after HT applied at 700 and 1000 °C, where an additional reduction of the CoF to 0.75 ± 0.035 and 0.63 ± 0.057 , is observed. These values correspond to reductions of 20.2% and 33%, respectively, compared to the pure Ti coating. This behavior indicates greater interaction between the GNPs and the Ti matrix, which improves load distribution and wear resistance [19,49,50].

These findings highlight the effectiveness of GNPs reinforcement in combination with HT to optimize the tribological properties of Ti coatings. However, the additional reduction of the CoF between HT at 700 and 1000 °C is limited, suggesting that the effects of the HT reach a saturation point at higher temperatures. This indicates that, although

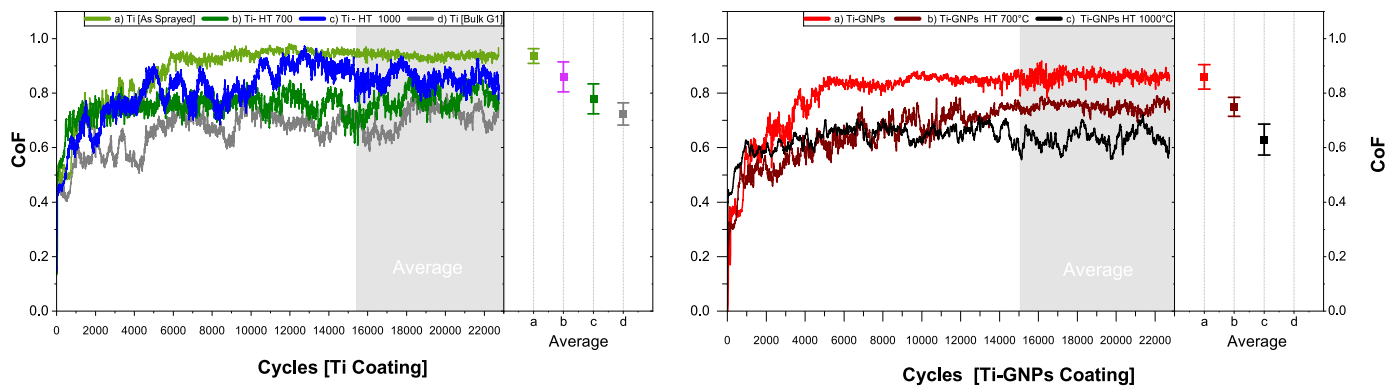


Fig. 11. CoF evolution of CS Ti and Ti-GNPs coatings.

HT improve the cohesion and integration between the GNPs and the Ti matrix, there is a limit to the optimization of the CoF by increasing the HT temperature.

4. Conclusions

By comparing the characteristics, properties, and behaviors of Ti and Ti-GNPs with 0.5 wt% GNPs coatings produced by CS in as-sprayed and after HT at 700 and 1000 °C, some conclusions can be drawn:

- The addition of GNPs in Ti powder significantly improves the deposit's mechanical properties due to enhancing the cohesion of Ti particles without severe microstructural changes. Ti-GNPs as-sprayed resulted in a σ_u of 184.81 MPa and E of 45.08 GPa, while pure Ti showed a σ_u 91.10 MPa and E of 29.39 GPa.
- The addition of GNPs in Ti powder significantly acts as a lubricant for a sliding wear loading, which is evidenced by the reduction of CoF from 0.94 to 0.69 in as-sprayed condition.
- The HT of Ti-GNPs coatings drastically improves the material properties by an augmentation of the cohesion of particles by diffusion mechanism. A top value of σ_u of 539.45 MPa and E of 76.36 GPa was achieved for HT at 1000 °C.
- Despite the positive results, exposing Ti-GNPs to elevated temperature, e.g., HT at 1000 °C, degrades the GNPs. It is supported by the appearance of defects in the carbon structures, according to Raman spectroscopy analysis. Furthermore, the formation of TiC, although beneficial for the hardness increasing, may be associated with the loss of the original crystalline structure of GR, suggesting that the optimization of the HT requires a careful balance to preserve the properties of GR.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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